Progress Report

TO

IOWA STATE HIGHWAY COMMISSION

TIME-TEMPERATURE STRENGTH -REACTION PRODUCT RELATIONSHIPS IN LIME-BENTONITE-WATER MIXTURES

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by

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SYNOPSIS

The interrelation of curing time, curing temperature, strength and reactions in lime-bentonite-water mixtures was examined. Samples were molded at constant density and moisture content and then cured for periods of from 1 to 56 days at constant temperatures that ranged from 5° C to 60° C. After the appropriate curing time the samples were tested for unconfined compressive strength. The broken samples were then analyzed by X-ray diffractometer and spectrophotometer to determine the identity of the reaction products present after each curing period.

It was found that the strength gain of lime-clay mixtures cured at different temperatures is due to different phases of the complex reaction, lime + clay → CSH(gel) → CSH(II) → CSH(I) → tobermorite. The farther the reaction proceeds, the higher the strength. There was also evidence of lattice substitutions in the structure of the calcium silicate hydrates at curing temperatures of 50° C and higher. No consistent relationship between time, temperature, strength, and the S/A ratio of reaction products existed, but in order to achieve high strengths the apparent C/S ratio had to be less than two.

The curing temperature had an effect on the strength developed by a given amount of reacted silica in the cured lime-clay mixture, but at a given curing temperature the cured sample that had the largest amount of reacted silica gave the highest strength.

Evidence was found to indicate that during the clay reaction some calcium is indeed adsorbed onto the clay structure rather than entering into a pozzolanic reaction.

Finally, it was determined that it is possible to determine the amount of silica and alumina in lime-clay reaction products by spectrophotometric analysis with sufficient accuracy for comparison purposes. The spectrophotometric analysis techniques used during the investigation were simple and were not time consuming.

INTRODUCTION

Lime and portland cement have been tested extensively to determine their efficiency in the stabilization of various soils. Portland cement pastes have also been thoroughly investigated to determine the mechanisms by which cementation occurs. Less investigation has been made of the soil-lime reaction, but what has been done indicates that the reaction products are similar to those formed during the hydration of portland cement. However, most of the work that has been done in determining the mechanism of the soil-lime reaction has been concerned with the effect of time on the strength of the soil-lime mixture, and the effect of time and/or temperature on the reaction products formed. Little attention has been given to the interrelation of time, temperature, and strength of lime stabilized soil.

The objective of this investigation is to study this interrelation of curing time, curing temperature, strength, and reactions in lime-clay mixtures. It will be noted that previous time-temperature-strength studies were done before lime-clay reaction products were known or identifiable, so it seemed appropriate to draw together these two paths of research, using one to explain or show the significance of the other.

REVIEW OF LITERATURE

Lime-Clay Reaction

The production of hydrates by a lime-clay reaction has been termed a "pozzolanic" reaction. A pozzolan is a siliceous or siliceous aluminous material which has little or no cementitious value, but will react with calcium hydroxide in the presence of moisture to form cementitious compounds (1, 23). A pozzolan can be either a natural or artificial material.

The beneficial effect of lime on the workability and strength of clayey soils has long been recognized. However, it is only in the past few decades that the

mechanisms by which this improved strength and workability are obtained have gradually become understood.

It now appears that the lime-clay reaction takes place in two steps. Davidson and Handy (6) suggest three basic reactions: first, the calcium ions cause a reduction in the plasticity of the clay; second, the lime may be carbonated by the carbon dioxide in the air resulting in the formation of a weak cement; and third, a cementitious reaction takes place between the lime and clay mineral. According to Hilt and Davidson (14) before any pozzolanic reaction takes place, the lime content of the lime-clay mixture must exceed the amount needed to modify the clay.

Studies made on the products of lime-clay systems have shown that calcium silicate and calcium aluminate hydrates are formed in various forms at temperatures ranging from room temperature up (9, 10, 13, 26, 44).

Several investigators have studied the strength characteristics of the calcium silicate hydrates and have characterized all the products as cementitious (19, 24, 28, 34, 40). Furthermore, the formation of calcium aluminate and calcium silicate hydrates during the hydration of portland cement is believed to be responsible for the strength and cementing ability of portland cement concrete (3, 5, 22), although the aluminates play a less significant role (3). The calcium silicate hydrate known as tobermorite gel, a poorly crystalline colloidal substance, has been called the "heart of concrete" (4). Jambor (18) found that the kind and microstructure of calcium silicate hydrate as well as the amount formed has an effect on the strength developed by hardened lime-pozzolana pastes.

Reaction Products

The major reaction products now recognized to be formed during the lime-clay reaction are tobermorite, CSH(I)[1], CSH(II), CSH(gel), calcium aluminate hydrates, and hydrogarnet (9,13,18,44).

The first four of these compounds are members of what is known as the tobermortie group of calcium silicate hydrates (36). The structure of tobermorite is similar to that of some clay minerals (25,39). All members of the tobermorite group, however, do not have precisely the same structure. These calcium silicate hydrates, in addition to the structural similarities, also have the small particle size, large surface area, and a number of other properties analogous to clay minerals (7,37).

Time, Temperature, Strength Interrelationship

As long ago as 1886 it was recognized that there was some relationship between curing temperature, curing time, and strength of portland cement and lime-sand cement (42). Since that time other investigators have studied the interrelation of strength, time, and temperature of concrete (3,29,30,31,35). Three principal approaches to the problem have been made. Bergström (2) suggested a "maturity" rule such that any given concrete would attain the same strength if $A(T - \theta)$ were constant. In this expression,

A = time of curing

T = curing temperature (C)

θ = the temperature at which no increase in strength occurs.

[1] It is customary in cement chemistry to denote the following compounds by short symbols: $CaO = C$; $SiO_2 = S$; $Al_2O_3 = A$; $Fe_2O_3 = F$; $MgO = M$; $H_2O = H$. Thus $nCaO \cdot pSiO_2 \cdot qH_2O$ is represented by CSH.

Plowman (30) modified this to the form:

$$UCS = \text{Constant} + \log A(T - \theta)$$

Rastrup (31), after studying the hydration process, based his "maturity" rule on the form:

$$UCS = f(T_a)$$

where

$$T_a = \int_o^A 2^{(T - \theta)/10} dA$$

T_a is the "maturity" at curing temperature T, after a curing time A.

The effect of curing temperature on the strength of soil-lime mixtures has also been studied (8, 27). It was found in these studies that the effect of increased curing temperatures was to increase the strength of the soil-lime mixtures at the same age. Metcalf (27) also showed that although none of the "maturity" rules above hold exactly for soil-lime mixtures, his results most nearly follow the rule proposed by Rastrup.

Metcalf (27) assumed that the reaction between lime or cement and clay could be represented by the Arrhenius equation:

$$k = B\, e^{-E/RT}$$

where k = the reaction rate

E = the activation energy

R = the gas constant

T = the temperature (in degrees Kelvin) and

B = constant

He then plotted his results on the basis:

$$\log (UCS) = B' - B''/T$$

where B' and B'' are constants

He found that the results of cement-stabilized soils plot a constant slope over the range 0-65 C, indicating that the hardening action in that temperature range is essentially similar and independent of the type of soil.

For lime-stabilized clays, however, Metcalf found not only was the slope of the curves different for the different clays but that there was an abrupt change of slope in the vincinity of 45°C. He made no comment concerning the change of slope at 45°C but did conclude that the lime-clay reaction responsible for the strength of the lime-clay mixture is not the same for all clay minerals.

PROCEDURES

Materials

The clay used in this investigation was a natural Ca-saturated "Panther Creek Southern Bentonite" from White Spring, Mississippi.

The lime used was a powdered analytical reagent grade calcium hydroxide.

Distilled water was used in the preparation of all specimens.

PREPARATION OF SPECIMENS

Molding

In order to reduce the variables to a minimum, only one ratio of lime to clay was examined. A C/S ratio of approximately 1.0 was chosen for the study because Wang (44) had established that this C/S ratio produced a variety of reaction products over the curing times and temperatures to be studied. The clay used in the investigation was chosen because some information concerning its reaction with lime had already been developed by Wang (44).

Proper amounts of lime, clay, and water were hand mixed until a uniform mixture was obtained; then the amount of material required to attain the maximum density was weighed out and placed in the mold. The specimens were molded into 1-in.-high by 1/2 in.-diameter cylinders and to constant density at optimum moisture content for maximum density.

The use of 1-in.-high by 1/2-in.-diameter strength-test specimens results in considerable savings of time and materials. The results obtained reflect the cohesive strength of the lime-clay system, and are sufficiently valid for comparative studies. The molding apparatus has been described in detail by Roderick (32).

Curing

After being molded, the samples were placed on a rack inside an airtight hard plastic Lustro-wave bowl in which distilled water had been so placed that the water was not allowed to come in contact with the specimens. The bowls were further sealed at the top with cellophane tape to prevent carbonation and the loss of moisture, before being placed in the appropriate curing chambers. Electric ovens were used as chambers for the 40°C, 50°C, and 60°C curing. The 23° C curing was performed in a temperature-controlled humidity room. The 5°C curing was done in a small laboratory refrigerator.

After completion of specified curing, the specimens were tested for strength by a proving ring type of compression apparatus, accurate to $\pm$ 25 psi, and the average of the five specimens was reported as the unconfined compressive strength.

Following the strength testing, all the broken samples of the same curing time and temperature were placed in a desiccator and vacuum dried over a mixture of $CaCl_2$ and Ascarite for a period of at least 48 hours. The dried samples were ground by hand to pass the No. 200 sieve and were stored for X-ray and chemical analyses.

X-ray Diffraction

A General Electric XRD-5 diffractometer and nickel-filtered copper Kα radiation were used for examining the presence of crystalline reaction products and for the determination of the unreacted calcium hydroxide in the cured mixtures.

The powder samples were pressed into disc-shaped brass rings with a 1000-psi presser to avoid effects of preferred orientation and to give good reproducibility (33). To further avoid the effects of preferred orientation, the discs were continually rotated while exposed in the X-ray beam (12).

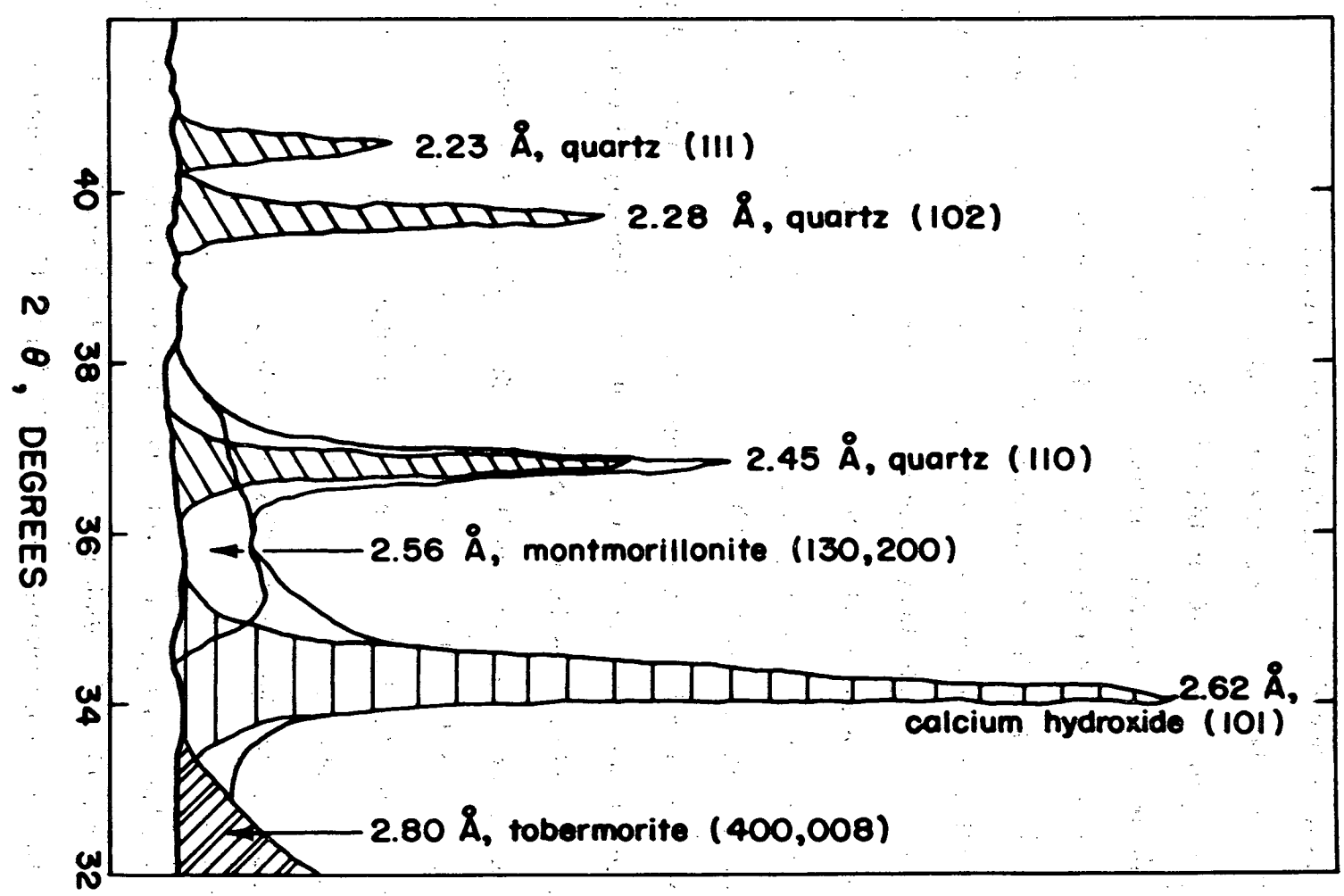
Determination of Calcium Hydroxide Content

The quantitative determination of the calcium hydroxide content of the cured mixture was made using the internal standard method outlined by Klug and Alexander (21).

Quartz powder was used as the internal standard. The standard series of mixtures used in preparation of the calibration curve was made up from finely ground quartz powder, calcium hydroxide, calcium carbonate, and the clay. The mixtures were placed in 4-gram glass vials with three small pieces of rubber and mixed in a Spex Model 8000 vibratory mixer/mill for five minutes to assure thorough mixing. Five samples of each mixture were then examined by X-ray analysis, and the intensities of the d = 2.62 Å (calcium hydroxide) and d = 2.45 Å (quartz) peaks were compared. Because of the linearity of the curves and the reproducibility of the data, it was not necessary to use additional mixtures.

In the determination of the intensities, allowances were made for the background intensity. Figure 1 shows a composite chart of the X-ray traces of quartz, calcium hydroxide, montmorillonite and tobermorite for copper Kα radiation from 32^{o} to 40^{o} 2θ; the background under the calcium hydroxide peak at approximately 34.1^{o} was assumed to be equal to the background at around 39^{o}. Similarly, the background under the quartz peak at 36.8^{o} was taken as a straight line connecting the background at 38.2^{o} and 35.9^{o}. These observations were used in the calculation

Figure 1. Composite chart of X-ray traces of quartz, calcium hydroxide, montmorillonite and tobermorite for copper $K\alpha$ radiation from 32^{o} to 40^{o} 2 θ.


2.23 Å, quartz (111)
2.28 Å, quartz (102)
2.45 Å, quartz (110)
2.56 Å, montmorillonite (130,200)
2.62 Å,
calcium hydroxide (101)
2.80 Å, tobermorite (400,008)
2 θ, DEGREES
40
38
36
34
32

of the intensities of the quartz and calcium hydroxide peaks as shown in Figure 2. A line was drawn connecting the intensity at 38.2° to the intensity at 35.9°, and the distance from the quartz peak to this line was considered the peak intensity of the quartz. Another line was drawn parallel to the intensity at 38.2°, and the distance from the calcium hydroxide peak to this line was considered the peak intensity of the calcium hydroxide. The heights were measured rather than areas, because observations showed that there was no appreciable difference in line broadening.

The quantitative analysis for calcium-hydroxide in the cured mixtures was carried out under the same conditions as the preparation of the calibration curves. In this case, 0.5 gram of ground quartz was mixed with 2.5 grams of the ground cured sample, and the calcium hydroxide content was found by comparison of the ratios of the intensities of the lines indicated above with those of the standard curve. The hygroscopic moisture content of the sample was determined, and the calcium hydroxide content was reported as grams per 100 grams oven-dry mixture.

Determination of Silica and Alumina Content

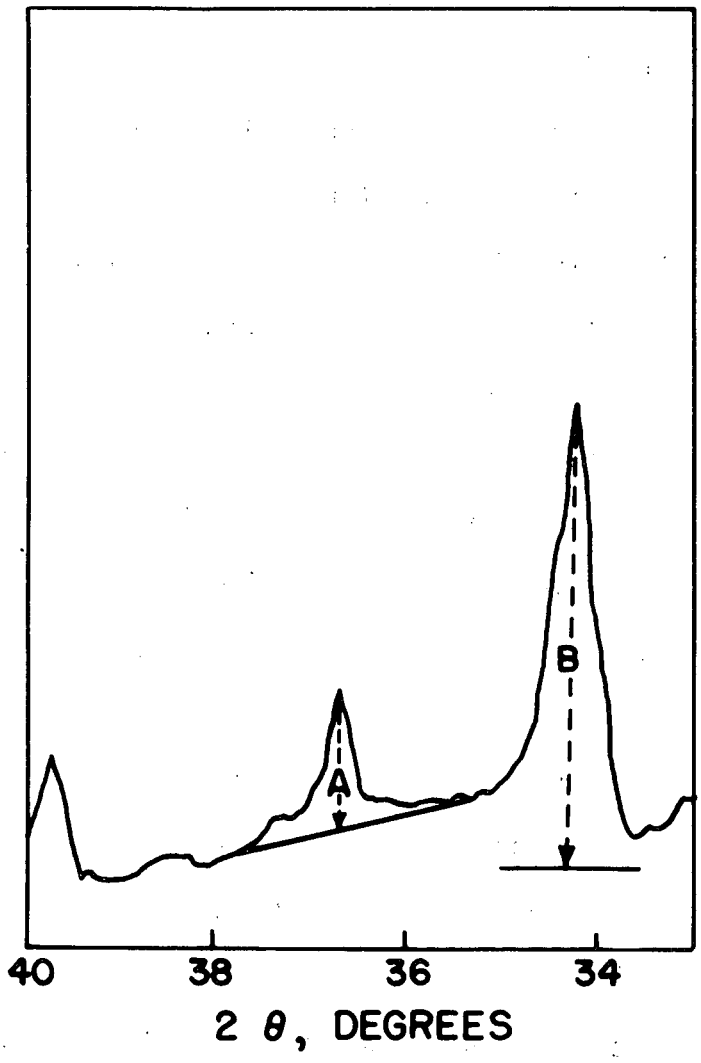
The amounts of silicates and aluminates formed in the reaction mixtures may be determined by chemical means because these reaction products are soluble in dilute HCl, whereas the solubility of the clay mineral is negligible under certain specified conditions (22).

Preliminary Tests for Optimum Conditions for Extraction

Time of Extraction

The procedure is designed to extract the maximum amount of Ca-silicates and aluminates formed with the minimum dissolution of clay minerals. Preliminary tests had shown that pure tobermorite synthesized from quartz and lime at 175° C in a saturated steam autoclave can be dissolved completely in a sufficient amount of 0.1 N HCl within 30 minutes by continuous shaking. It also had been shown that clay

Figure 2. Example of calculation of the intensities of the quartz and calcium hydroxide peaks.


A
B
40
38
36
34
2 θ, DEGREES

or soil samples are not subjected to any extensive breakdown under this condition.

Proper Concentration of HCl. The reaction products must be dissolved in HCl of such strength as to give a final supernatant pH of between 1 and 2. The pH is critical for two reasons. First, the rate of polymerization of silicic acid dissolved is a minimum in this pH range (17). Second, the aluminum ion is stable at this pH range, but slowly polymerizes and precipitates as $Al(OH)_3$ at a pH greater than 4.5. In addition, the strength of the HCl must be such that all the calcium silicates and aluminates are dissolved and at the same time a minimum amount of clay is dissolved. The optimum strength of the HCl used for extraction varies depending on the clay and the lime content of the lime-clay mixture. To determine the optimum acid strength for the lime-clay mixture used to the present investigation, a series of tests was made by shaking 0.5 gram of the sample in 50 ml HCl for 30 minutes.

From the results of these tests, it was decided that an acid concentration of 0.20 N and a 30-minute shaking time best met the criteria.

Sample Extraction. A suspension of 0.5 gram sample in 50 ml of 0.2 N HCl was placed in a 125-ml Erlenmeyer flask and was shaken for 30 minutes on a vibratory shaker operated at approximately 400 rpm. The residue was then immediately washed into a 50-ml centrifuge tubes and centrifuged at 16,000 rpm for 10 minutes to obtain a clear supernatant, which was then diluted to 100 ml with distilled water in a 100-ml volumetric flask.

Alumina Determination. Modifying the procedure for determination of aluminum outlined by Vogel (42), a quantity of extract containing between 0.01 and 0.10 mg of aluminum in a 25-ml volumetric flask was treated with 5 ml of a buffer solution, made up of 77 grams NH_4AC and 57 ml concentrated HAC per liter to give a pH of 4.5. One ml of 0.2-percent freshly prepared Aluminon reagent was added, and the

mixture made up to 25 ml with distilled water and allowed to stand for 30 minutes before the color intensity was measured at 520 mμ on a Beckman Model B spectrophotometer. A calibration curve was prepared in exactly the same manner by using a standard solution made up of $AlK(SO_4)_2 \cdot 12\ H_2O$ to contain 0.01 mg/ml of aluminum. The aluminum content in each sample was determined from the calibration curve and was expressed in grams of alumina per 100 grams of oven-dry mixture.

Silica Determination. Following the procedure outlined by Govett (11), an aliquot of extract containing between 0.2 mg and 0.7 mg SiO_2 was added to a 25-ml volumetric flask acidified with 5 ml of 1 N H_2SO_4 and further treated with 5 ml of 0.3-M (with respect to $MoO_4)^{-2}$) ammonium molybdate. The sample was then made up to 25-ml volume with distilled water. The color intensity was measured at 400 mμ on a Beckman Model B spectrophotometer not sooner than two minutes nor later than ten minutes after the addition of ammonium molybdate. The standard silica solution was prepared by dissolving sodium metasilicate ($Na_2SiO_3 \cdot 9\ H_2O$) in distilled water acidified with H_2SO_4 to give the final pH about 1.5. Aliquots of the standard solution containing 0.1 to 1.0 mg SiO_2 per 25 ml. were used to prepare the standard curve exactly the same manner as above. The silica content was determined from the standard curve and was reported in grams per 100 grams oven-dry mixture.

RESULTS AND DISCUSSION

Strength vs. Time

No significant loss of moisture was found in any of the samples cured at 5°C, 23°C, and 40°C up to 56 days; 50°C up to 28 days; and 60°C up to 14 days. Samples cured at 50°C for 56 days and at 60°C for 28 and 56 days seemed excessively dry, and the containers were completely dry. This lack of excess water is believed to have critical effects on the strengths obtained and the formation of reaction products; therefore, data on the samples cured at those temperatures for those times were ignored.

Figure 3 shows the average and extreme unconfined compressive strengths as a function of curing time for the various curing temperatures. Except for the 3-day curve at 5°C, the figure shows an increase of strength with time at all temperatures with the greater rate of increase at the higher temperatures. This was as expected. The drop in strength for 3-day curing at 5°C appears to be due to experimental error.

Figure 4 shows the unconfined compressive strength as a function of log T_a; with $T_a = 2^{(T + 11.7)/10}A$, where T = curing temperature in degrees centigrade and A = curing time in days. This function of time and temperature was chosen because Metcalf (27) showed that of all the "maturity" laws, this one gave the closest fit to the results of lime-clay stabilization. The T_a used in this expression is merely a simplification of Rastrup's (31) "maturity" rule, $T_a = \int_o^A 2^{(T - \theta)/10} dA$, when the temperature at which the reaction ceases is considered to be -11.7°C and the curing takes place at a constant temperature during the entire curing time. The temperature -11.7 C was chosen because Plowman (30) determined this temperature to be the datum temperature for concrete maturity calculations. Saul (35) had earlier chosen -10C for the datum on the basis of curve fitting. Plowman made his modification on the basis of direct measurements. A plot of the unconfined compressive strengths of the present investigation was made using -10°C as the datum temperature, and it was found that there was a great deal more scattering of points than when the -11.7°C datum temperature was used. However, even with the increased scatter, the -10° C datum temperature plot had all the characteristics of Figure 4. Examination of Figure 4 shows a grouping of points along two different lines. The lower line is formed by the unconfined compressive strengths of samples cured at 5° C and 23° C; the upper line by the unconfined compressive strengths of the samples cured at 40°C, 50°C, and 60° C. Plotting the average unconfined compressive strength as log (UCS) = B' - B''/T in the fashion of Metcalf (27), Figure 5 shows a similar trend.

Figure 3. Relation between unconfined compressive strength and curing time for lime-clay mixtures cured at various temperatures.

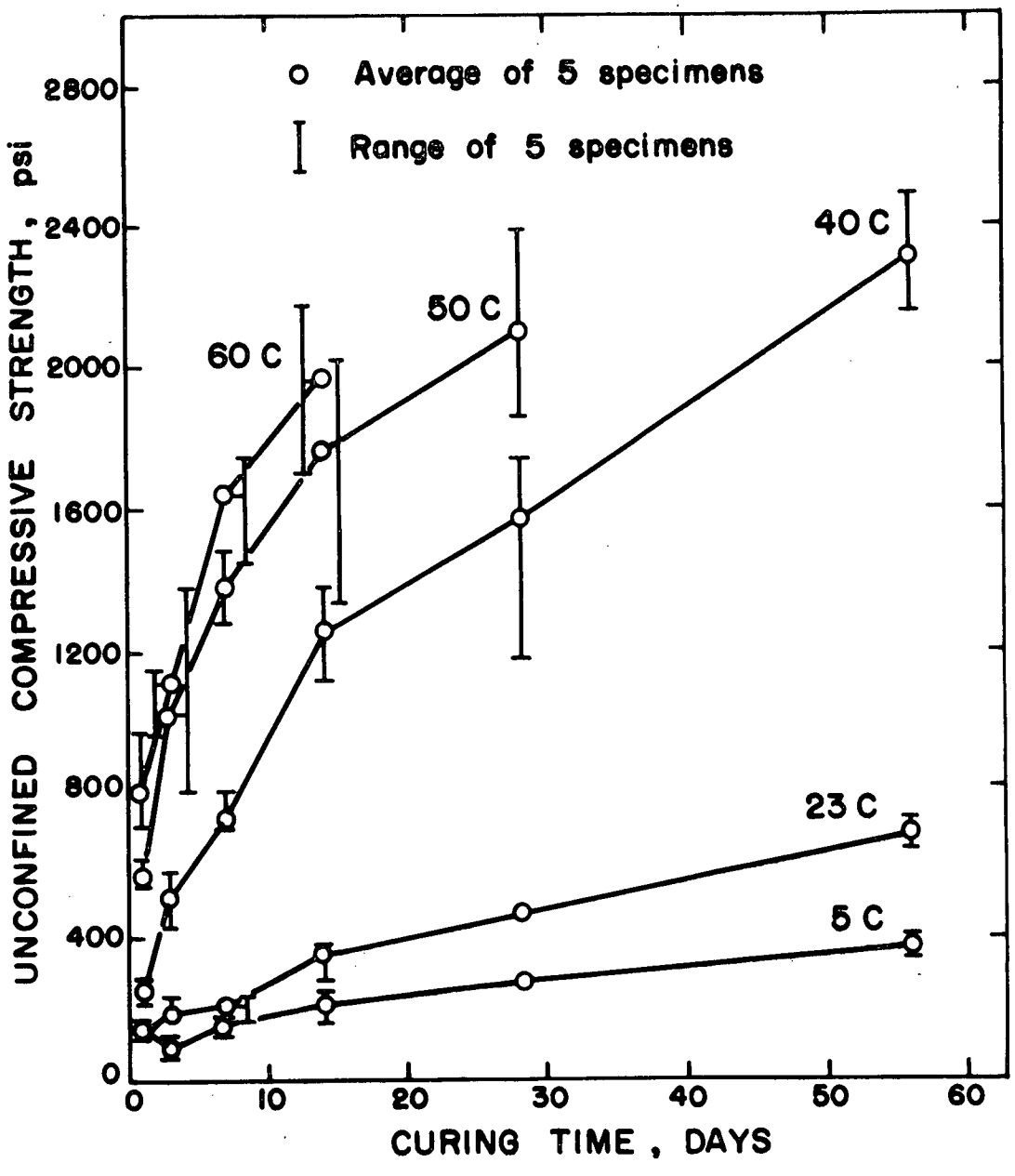

Average of 5 specimens
Range of 5 specimens
UNCONFINED COMPRESSIVE STRENGTH, psi
2800
2400
2000
1600
1200
800
400
0
0
10
20
30
40
50
60
CURING TIME, DAYS
40 C
50 C
60 C
23 C
5 C

Figure 4. Relation between unconfined compressive strength and "maturity".

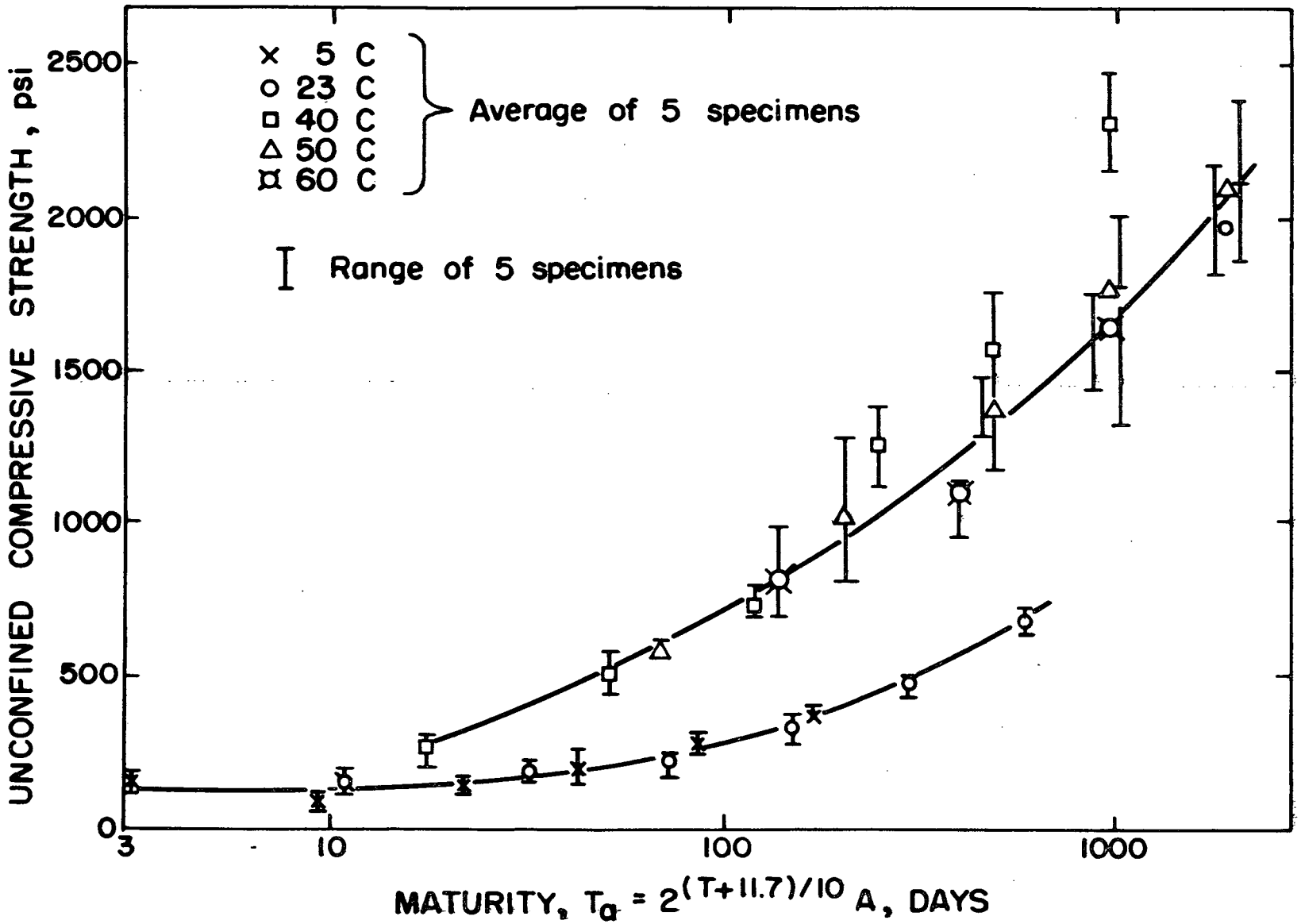
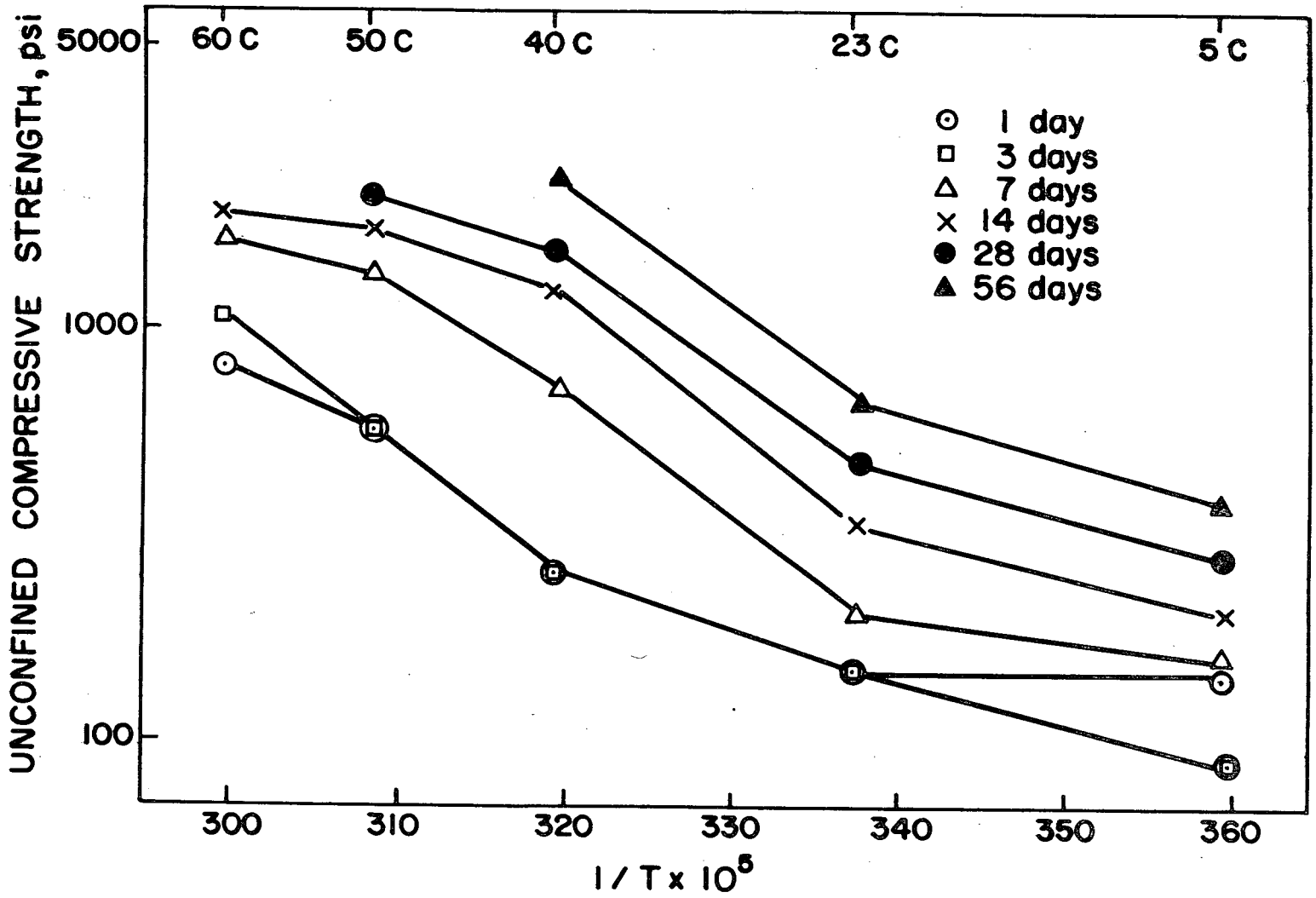

× 5 C
○ 23 C
□ 40 C
△ 50 C
⌑ 60 C
Average of 5 specimens
Range of 5 specimens
UNCONFINED COMPRESSIVE STRENGTH, psi
2500
2000
1500
1000
500
0
3
10
100
1000
MATURITY, $T_a = 2^{(T+11.7)/10} A$, DAYS

Figure 5. Relation between unconfined compressive strength and temperature after various curing times.


UNCONFINED COMPRESSIVE STRENGTH, psi
5000
1000
100
60 C
50 C
40 C
23 C
5 C
1 day
3 days
7 days
14 days
28 days
56 days
300
310
320
330
340
350
360
1/T x 10^6

Taking equal slopes to indicate that the strength is due to a similar reaction, some observations can be made. It appears that three distinct reactions can be identified. The first is produced for 7-, 14-, 28-, and 56-day curing in the range 5-23°C, 3-day curing in the range 5-40°C, and 1-day curing in the range 23-40° C. A second is produced for 1-day curing in the range 40-50°C, 3-day curing in the range 40-60°C, 7-day curing in the range 23-50°C, and 14-, 28-, and 56- day curing in the range 23-40°C. The third is produced for 1- and 7-day curing in the range 50-60°C, 14-day curing in the range 40-60°C, and 56-day curing in the range 40-50° C.

One explanation is that a different reaction product is formed at different curing temperatures and that the cutoff temperature lies between 23° C and 40°C. With the same materials used in this investigation and C/S = 0.892, Wang (44) found that the mixtures produced CSH (gel), CSH(I), hydrogarnet and C_4AH_{13} when cured at 40° C for periods of 7 to 180 days, the products formed being dependent on the curing time. The same mixture composition cured at 23°C for periods of from 28 to 180 days produced only CSH(gel) and C_4AH_{13}. Glenn (9) also found, when investigating a similar bentonite-lime mixture with C/S = 0.69, that mixtures cured at room temperature for long periods produced C_4AH_{13}, CSH(I), CSH(gel), and possibly CSH(II). Mixtures of the same composition cured for short periods at higher temperatures yielded; CSH(gel), CSH(I), and C_4AH_{13} at 40°C; and CSH(I), and possibly CSH(II) or aluminum substituted tobermorite at 80°C.

A sequential reaction is suggested by Taylor (37) for lime-quartz pastes; he states that although many details of the reaction are obscure and others depend on the conditions of the investigation, the general picture seems to be clear: Reactions on the quartz surface initially give a lime-rich substance similar to CSH(II).

When the overall C/S ratio is low, this reaction proceeds until all the lime is depleted; the CSH(II) then reacts with more quartz giving CSH(I), the C/S ratio of which eventually drops to 0.8. If the temperature and time are sufficient, the CSH(I) then recrystallizes to tobermorite. If the overall C/S ratio is below 0.8, the CSH(I) or tobermorite also reacts slowly with the unused quartz to give gyrolite.

If the lime-clay reaction is similar to the lime-quartz reaction, and on the basis of reaction products it appears that it is, then it would appear that a complex reaction is taking place. It also appears that this complex reaction is a consecutive reaction of the form $A + B \xrightarrow{k} C \xrightarrow{1} D$, in which k is the rate constant for the first step and 1 is the rate constant for the second step (20). With $1 \geq k$ no C will be formed, and if $1 \ll k$ is negligible amount of D will be formed. Since k and 1 are temperature dependent, at some temperature where k is slightly higher than 1, both C and D will be present. As time progresses the amount of D will build up whereas the amount of C will increase slower. Now if D contributes more to the strength of the mixture than does C, at some time when the amount of D in the mixture is great enough, the mixture will behave as though all of its strength was coming from D. At temperatures around room temperature and below only the first reaction would be taking place; at temperature of 40° C and higher the second reaction will be taking place at relatively the same rate as the first, so that essentially there is very little if any of the first product formed.

In general, this consecutive reaction theory may be substantiated by data from Wang (44), who showed that CSH(gel) formed at short curing times and low temperatures, and converted to another CSH phase with prolonged curing.

Figure 3 also confirms that although the strength gain of the lime-clay mixtures cured at different temperatures appears to be due to different phases of the complex reaction, it may be possible to utilize accelerated curing methods to approximate

the strengths of soil-lime mixtures cured at lower temperatures for longer times. However, care must be exercised in the use of accelerated curing tests. Each soil that is to be subjected to accelerated curing should be investigated thoroughly to assure that disproportionate strengths are not achieved by accelerated curing.

Reaction Products

The discussion of the reaction products formed in the mixtures will be made on the basis of X-ray diffraction curves and data obtained from the spectrophotometric analysis of dilute HCl extract. The results will be discussed according to the curing times.

Figure 6 shows the acid-soluble alumina for samples cured at various temperatures for various times, corrected for the 0.13 grams alumina dissolved from the natural clay.

Figure 7 shows the acid-soluble silica for samples cured at various temperatures for various times, corrected for the 0.06 gram silica dissolved from the natural clay.

One-Day Curing. The X-ray diffraction curves for one-day curing confirm that reaction products in the tobermorite hydrate group are formed at all temperatures, indicated by peaks at 3.07 and 1.82 Å. All curing temperatures also produce a slight amount of C_4AH_n, indicated by peaks in the regions of 7.5, 4.1, 3.99, and 2.88 Å. However, the mixture cured at 23° C gives the most definite peak in the region of 7.5 Å. The mixture cured at 60° C also has broad weak peaks at 3.03 and 1.97 Å. The additional peak at 3.03 Å probably indicates that there are two phases of the tobermorite group present in the cured mixture, i.e., CSH(II) and CSH(gel). The 1.97 Å peak corresponds to a peak found by Diamond (7) in iron or magnesium substituted tobermorite; since no data are available on lattice substitution in CSH(II) or CSH(gel), this may indicate that some substitution is taking place in one or both of these.

Figure 6. Acid-soluble alumina in sample after curing at various temperatures for various times.

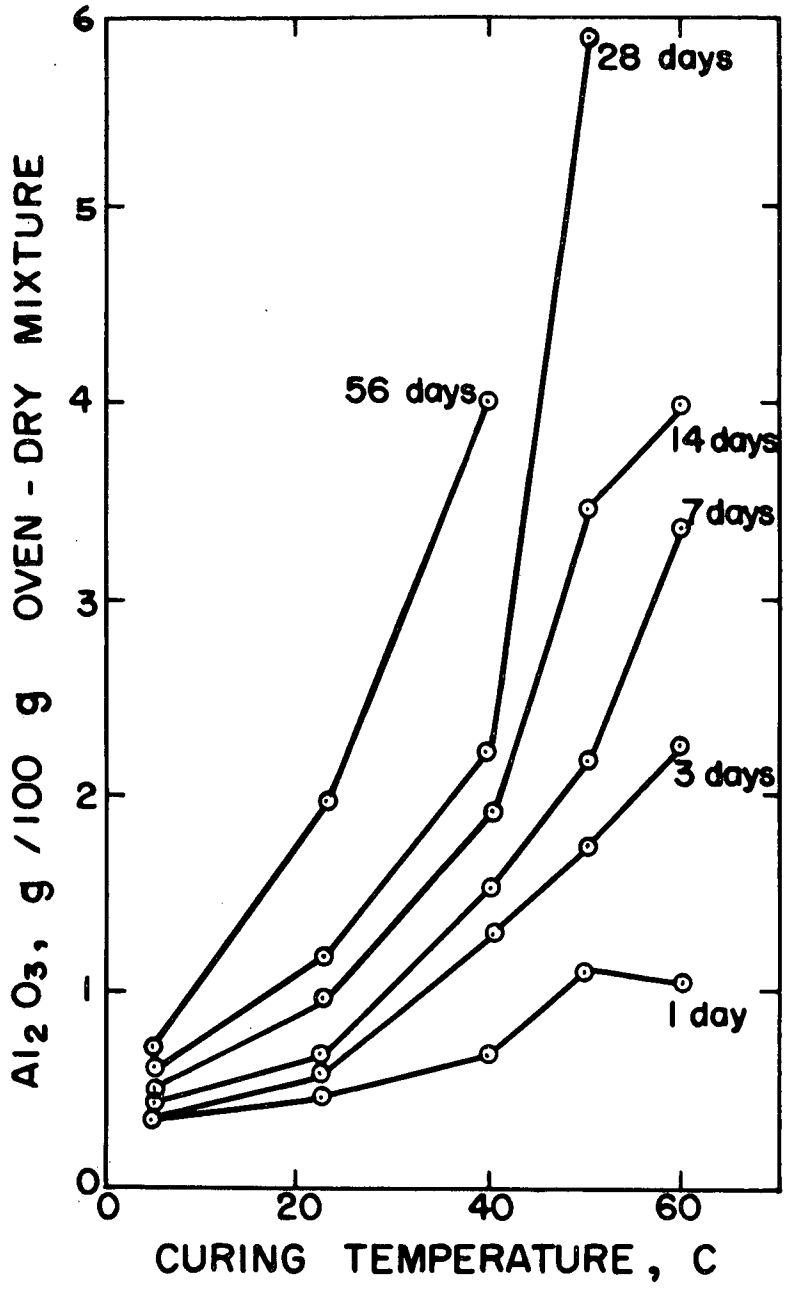
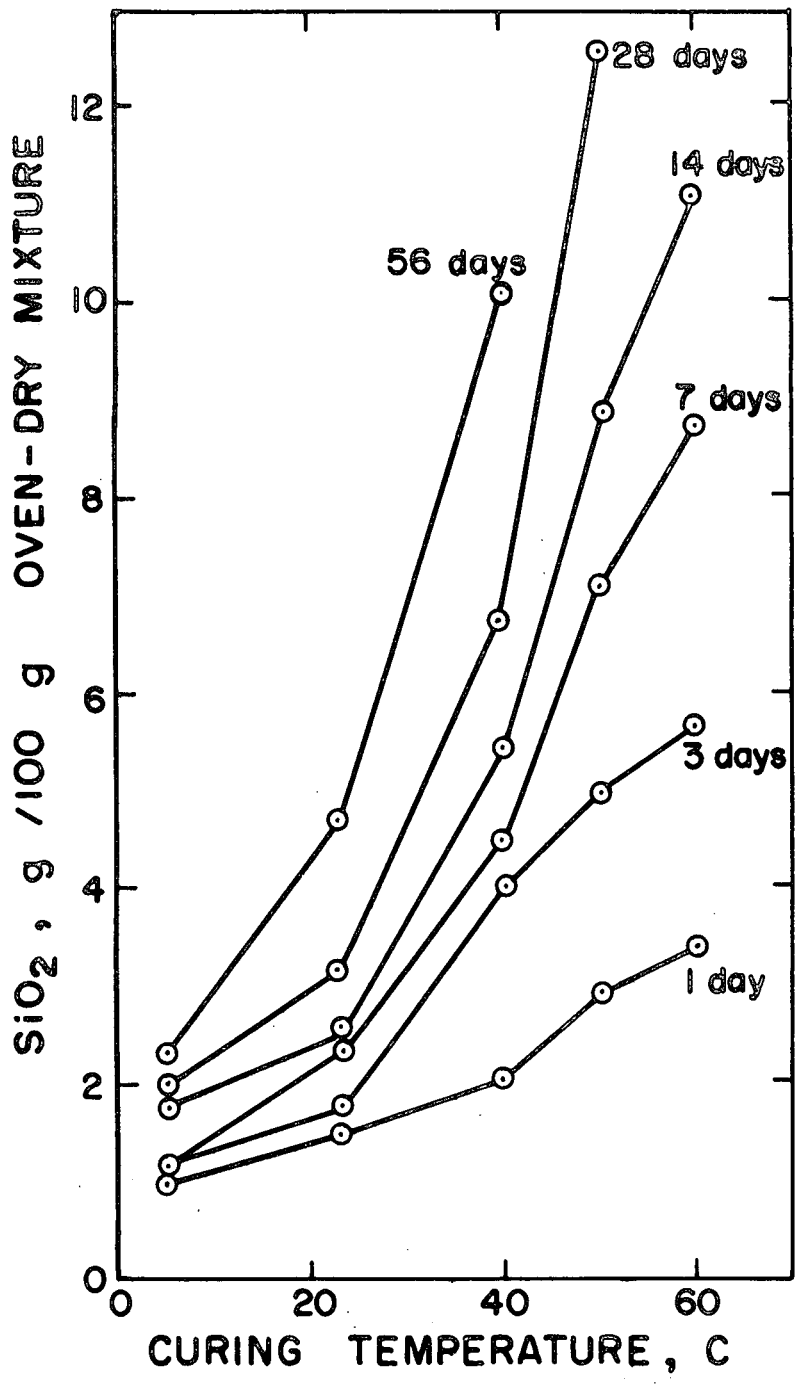

6
5
4
3
2
1
0
0
20
40
60
28 days
56 days
14 days
7 days
3 days
1 day
Al2O3, g /100 g OVEN - DRY MIXTURE
CURING TEMPERATURE, C

Figure 7. Acid-soluble silica in sample after curing at various temperatures for various times.


28 days
14 days
56 days
7 days
3 days
1 day
SiO_2, g /100 g OVEN-DRY MIXTURE
0
2
4
6
8
10
12
0
20
40
60
CURING TEMPERATURE, C

At one-day curing there is little difference in the amount of acid-soluble silica and alumina found after curing at 5°C and that found after curing at 60°C (Figures 6 and 7).

Three-day Curing. The X-ray diffraction curves for three-day curing are essentially the same as those for one-day curing, except that mixtures cured at all temperatures have weak peaks in the region of 10.5 - 9.8 Å, indicating the presence of CSH(II). The diagnostic 7.5Å peak is missing from all curves, but the other C_4AH_n peaks, although weak, are still present. The 1.97 Å peak does not appear in any of the curves, but there is a borad hump in the region of 3.03 Å on all curves. The rate of increase of acid-soluble alumina and silica with respect to temperature is slightly greater in samples at this curing time than it was in those in one-day curing (Figures 6 and 7).

Seven-day Curing. The X-ray diffraction curves of this curing time are the same as those for three-day curing; however, the 7.5 Å peak of C_4AH_n is quite evident at 50°C and 60°C curing temperatures, but not at the lower temperatures. At these same curing temperatures the 1.98 Å peak reappears, indicating possible iron or magnesium substitution in the calcium silicate hydrate. The rate of increase in acid-soluble alumina with respect to temperature is approximately constant between 23°C and 50°C but increases between 50 and 60°C (Figure 6). The rate of increase in acid-soluble silica is constant from 5°C and 40°C but increases from 40°C to 50°C and then decreases slightly between 50°C and 60°C (Figure 7). The latter may be another indication of lattice substitution.

Fourteen-day Curing. The X-ray diffraction curves again are the same as those for seven-day curing. A noticeable feature though is the change in shape of the curves for 50°C and 60°C curing temperatures at 3.07 Å. At shorter curing times this peak was relatively sharp, but now it has become very broad. At 60°C curing

temperature, additional peaks at 2.74 and 2.23 Å occur. The 2.74 Å peak is between a 2.78 Å peak reported by Diamond (7) for CSH(I) and a 2.7 Å peak also reported by him for aluminum-substituted tobermorite. The 2.23 Å peak was not accounted for.

Twenty-eight-day Curing. The diffraction curve for 50° C curing is the same as that of 60° C curing for 14 days, but the curves for other curing temperatures do not exhibit any change from the 14-day curves. It should be noted that there is a great increase in the rate of increase of acid-soluble silica and alumina between 40° C and 50° C (Figures 6 and 7).

Fifty-six-day Curing. The X-ray diffraction curves for 56-day curing are the same as those for 28-day curing except that very distinct peaks appear on all curves in the region of 7.5 Å, indicating the definite formation of crystalline C_4AH_n.

Summary of X-ray Data. No evidence of formation of hydrogarnet, ordinarily shown by peaks in the region of 2.68, 3.00, and 1.61 Å, was found in any of the X-ray diffraction curves.

A summary of the crystalline products diagnosed from X-ray diffraction are shown in Table 1. C_4AH_n is reported as present only where there are peaks in the region of 7.5 Å; at other times it is reported as probable, on the basis of other peaks.

At 5° C, 23° C, and 40° C curing temperatures C_4AH_n, CSH(gel) and CSH(II) appear to be the stable phases. The same products appear at 50° C and 60° C curing temperatures, with probable lattice substitutions and CSH(I) appearing after several days of curing.

Examination of Table 1 also reveals that the X-ray diffraction curves gave supporting evidence to the theory advanced earlier, that the lime-clay reaction is a consecutive reaction:

$$\text{lime} + \text{clay} \longrightarrow \text{CSH(gel)} \longrightarrow \text{CSH(II)} \longrightarrow \text{CSH(I)}$$

TABLE I

SUMMARY OF CRYSTALLINE PRODUCTS OBSERVED FROM X-RAY ANALYSIS

Curing Temp. °C	Curing Time					
	1 Day	3 Days	7 Days	14 Days	28 Days	56 Days
5	A?, G	A?G, II	A?, G, II	A?, G, II	A?, G, II	A, G, II
23	A, G,	A?G, II	A?, G, II	A?, G, II	A?, G, II	A, G, II
40	A?, G	A?G, II	A?, G, II	A?G, II	A?, G, II	A, G, II
50	A?, G	A?G, II	A, Ga, IIa	A, Ga, IIa	A, Ga, Ia, IIa	N. D.
60	A?, Ga, IIa	A, G, II	A, Ga, IIa	A, Ga, Ia, IIa	N. D.	N. D.

A - C_4AH_n

G - CSH(gel)

I - CSH(I)

II - CSH(II)

? - Probable

a - Probable Lattice substitution

N.D. - Not determined

as evidenced by the trend indicated in the 50° C and 60° C curing; and that at any given time there may be more than one phase of the reaction present, depending upon the curing time and temperature.

C/S Ratio of Reaction Products. Table 2 shows the apparent C/S ratio of the reaction products at the different curing times and temperature, based on the results of the X-ray diffraction determination of calcium hydroxide in the cured mixture, and the spectrophotometric determination of acid-soluble silica and alumina. These C/S ratios were computed after making these assumptions:

1. All the calcium hydroxide that disappears during curing is assumed to enter into the pozzolanic reaction.
2. All acid-soluble alumina is assumed to come from C_4AH_n reaction products.

The first assumption may be incorrect if as Hilt and Davidson (14) have shown, some of the lime is utilized in the modification of clay and does not enter into the pozzolanic reaction. Ho and Handy (15,16) have further shown that this lime does not show up on DTA curves, suggesting that the lime is adsorbed onto the clay structure. Since the exact amount of lime utilized in this manner could not be determined, the assumption was made to make a rough comparison rather than an exact determination of the reaction products' C/S ratio.

The second assumption may also be in error because of the indication of lattice substitution in the reaction products. However, since the amount and type of substitutions that do occur cannot be accurately determined, the assumption was considered valid enough for comparison purposes. The assumption of formation of only C_4AH_n products seems valid on the basis of X-ray analysis and the fact that in this temperature range the tetracalcium aluminate hydrates are most likely to be formed (41).

TABLE 2

C/S RATIO OF DISSOLVED REACTION PRODUCTS AFTER ASSUMING ALL ACID-SOLUBLE ALUMINA COMES FROM C_4AH_n PRODUCTS AND ALL CALCIUM HYDROXIDE THAT DISAPPEARS IS UTILIZED IN CALCIUM SILICATE AND CALCIUM ALUMINATE PRODUCTS

Curing Temp. °C.	Curing Time					
	1 Day	3 Days	7 Days	14 Days	28 Days	56 Days
5	6.0	6.2	6.6	4.7	5.8	3.8
23	3.4	3.8	2.6	3.6	3.2	2.7
40	2.6	1.9	1.7	1.7	1.8	1.5
50	2.7	1.7	1.7	1.6	.9	-
60	2.9	1.8	1.2	1.3	-	-

Except after one day of curing, the C/S ratios of the reaction products of the mixtures cured at 40°C, 50°C, and 60°C are all in the range 0.9 to 1.0, Table 2. Ratios of the mixtures cured one day, or those cured longer at 5°C and 23°C are much higher, 2.6 to 6.6. The reported C/S ratio of the tobermorite group of calcium silicate hydrates is in the range of 0.8 to 2.0 (38).

The validity of the first assumption is indeed questionable at low curing temperatures and short curing times, as the apparent C/S ratio is much higher than is believed possible for the tobermorite group (Table 2). Indeed, it is so much higher that it seems reasonable to take this as additional evidence that an appreciable amount of calcium is adsorbed onto the clay structure as suggested by Ho and Handy (15, 16). At higher temperatures and longer curing times this effect is reduced because of the dissolution of the clay and the accompany release of the adsorbed calcium. Otherwise the apparent C/S ratios of the reaction products closely correspond to those expected from the X-ray analysis, i.e., of the order of 0.8 to 2.0.

S/A Ratio of Reaction Products. Table 3 gives the ratio of acid-soluble silica to acid-soluble alumina at the different curing times and temperatures. Plots of these data against time, temperature, and unconfined compressive strength showed no consistent relationship except that all values of S/A are between 3.6 and 5.9 (Figure 8). The average is 4.76, or about identical with the S/A ratio of the clay, which is 4.75. The close agreement of the S/A ratio of the dissolved reaction products to the S/A ratio of the clay also indicates that the chemical determination of the acid-soluble silica and acid-soluble alumina is valid.

Relation of Strength of Reaction Products

Jambor (18) has shown that the compressive strength of a mixture is affected by the volume, and microstructure of the cementitious hydration products developed.

Figure 8. Relation of unconfined compressive strength to the S/A ratio of acid-soluble reaction products.

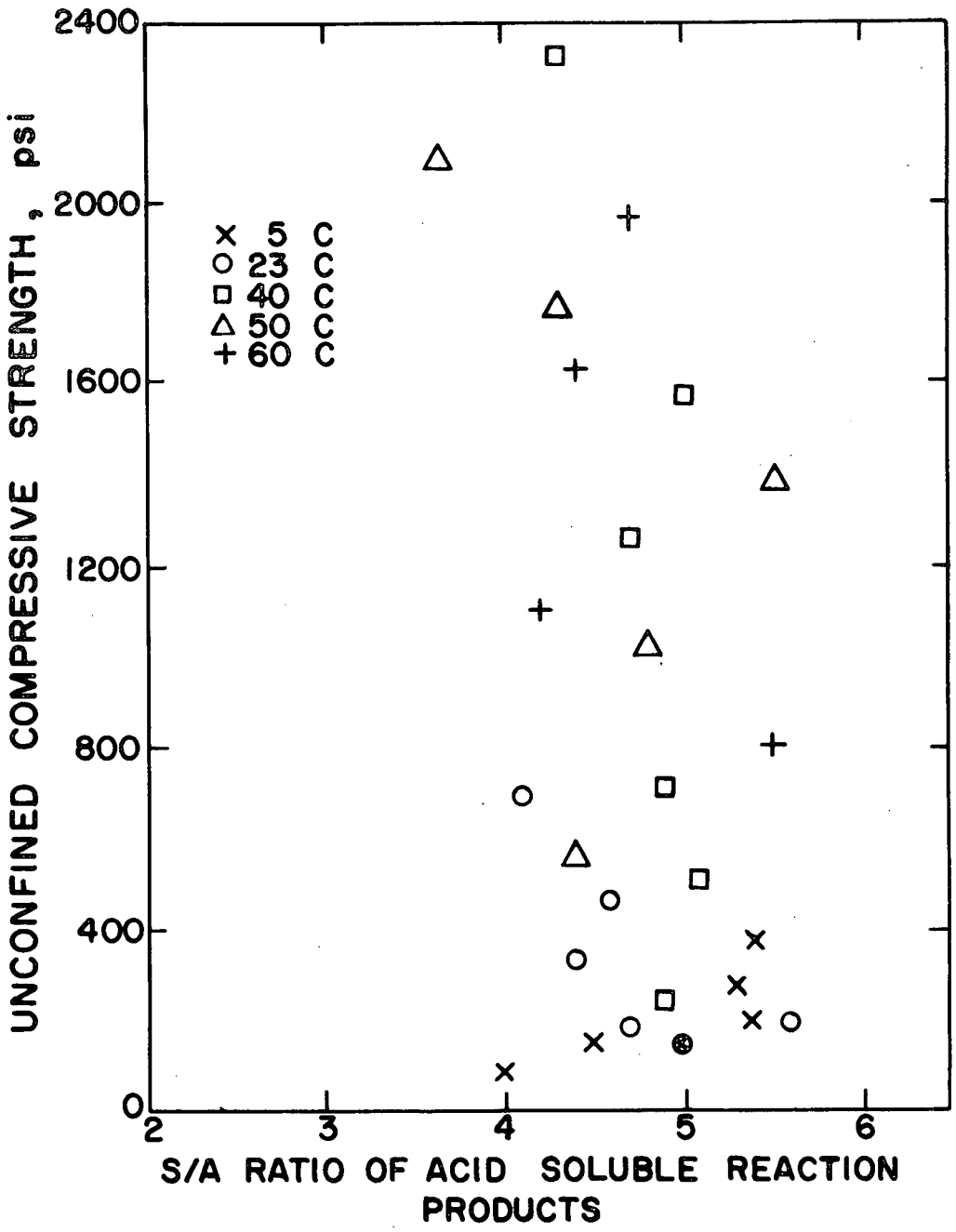

UNCONFINED COMPRESSIVE STRENGTH, psi
2400
2000
1600
1200
800
400
0
2
3
4
5
6
× 5 C
○ 23 C
□ 40 C
△ 50 C
+ 60 C
S/A RATIO OF ACID SOLUBLE REACTION PRODUCTS

TABLE 3

S/A RATIO OF ACID-SOLUBLE REACTION PRODUCTS AT VARIOUS CURING TIMES AND TEMPERATURES

Curing Temp °C	Curing Time						
	1 Day	3 Days	7 Days	14 Days	28 Days	56 Days	Avg.
5	5.0	4.0	4.5	5.4	5.3	5.9	5.02
23	5.0	4.7	5.6	4.4	4.6	4.1	4.73
40	4.9	5.1	4.9	4.7	5.0	4.3	4.82
50	4.4	4.8	5.5	4.3	3.6	-	4.52
60	5.5	4.2	4.4	4.7	-	-	4.70
Avg.	4.96	4.56	4.98	4.70	4.62	4.77	4.76

With this in mind let us examine the relationships, if any, of the various factors that have been determined in the investigation to the unconfined compressive strength of the cured mixtures.

As can be seen from Figure 9, the S/A ratio of reaction products has little or no effect on the strength of the cured mixture.

Figure 9 shows the unconfined compressive strength of the mixture as a function of the calcium hydroxide present in the cured samples. It is evident that the strength of the mixture is not a function of the calcium hydroxide alone, but that the temperature of curing has an effect on the strength of the mixture developed by the reaction of a given amount of calcium hydroxide. It is also evident that in the samples cured at 5° C and 23° C, the difference in temperature has little effect on the strength developed by the amount of disappearing calcium hydroxide. The same feature is noted in the samples cured at 40°C, 50°C, and 60° C. However, there is a noticeable difference in the strength developed by the disappearance of a given amount of calcium hydroxide between samples cured at 23°C and 40°C.

Figure 10 shows the unconfined compressive strength as a function of acid-soluble silica. Here again it appears that temperature plays a role in determining the strength developed by a given amount of silica. The samples cured at 5°C and 23°C follow one curve, the samples cured at 50° C and 60° C follow another, and the samples cured at 40°C follow still another.

Figure 11 shows the unconfined compressive strength as a function of acid-soluble alumina. The figure displays the same characteristics as Figure 10.

On the basis of these figures it can only be concluded that at a given curing temperature the cured sample that has the largest amount of acid-soluble silica or alumina, or the smallest amount of unreacted calcium hydroxide, will have the highest unconfined compressive strength. These figures also confirm that there is a

Figure 9. Relation between unconfined compressive strength and calcium hydroxide in cured samples. Prior to curing, the samples all contained 41.6 gm $Ca(OH)_2$ /100 gm oven-dry mixture, giving a C/S ratio of about 1.0.

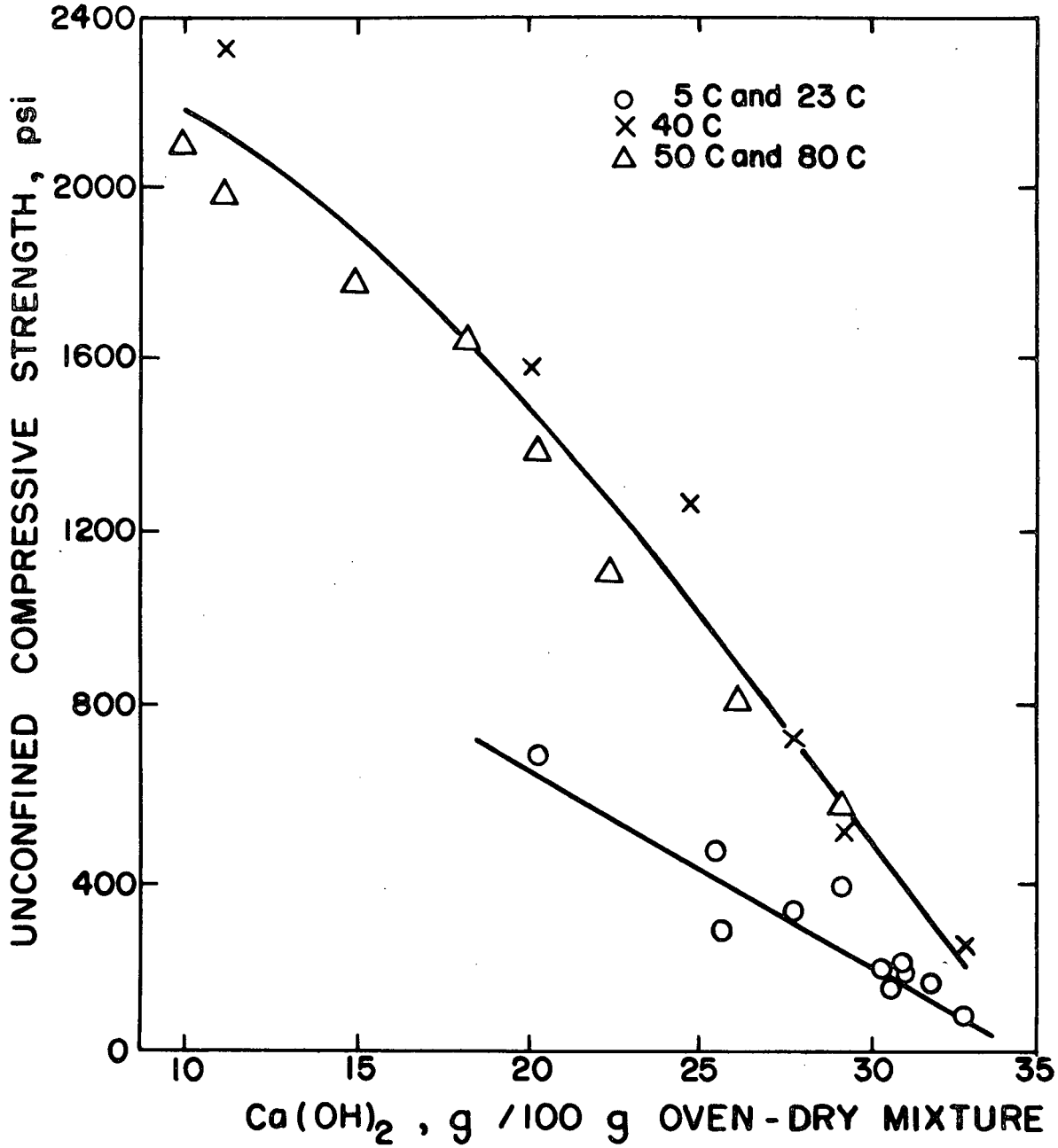

2400
2000
1600
1200
800
400
0
10
15
20
25
30
35
UNCONFINED COMPRESSIVE STRENGTH, psi
Ca(OH)2 , g /100 g OVEN-DRY MIXTURE
5 C and 23 C
40 C
50 C and 80 C

Figure 10. Relation between unconfined compressive strength and acid-soluble silica in cured samples.

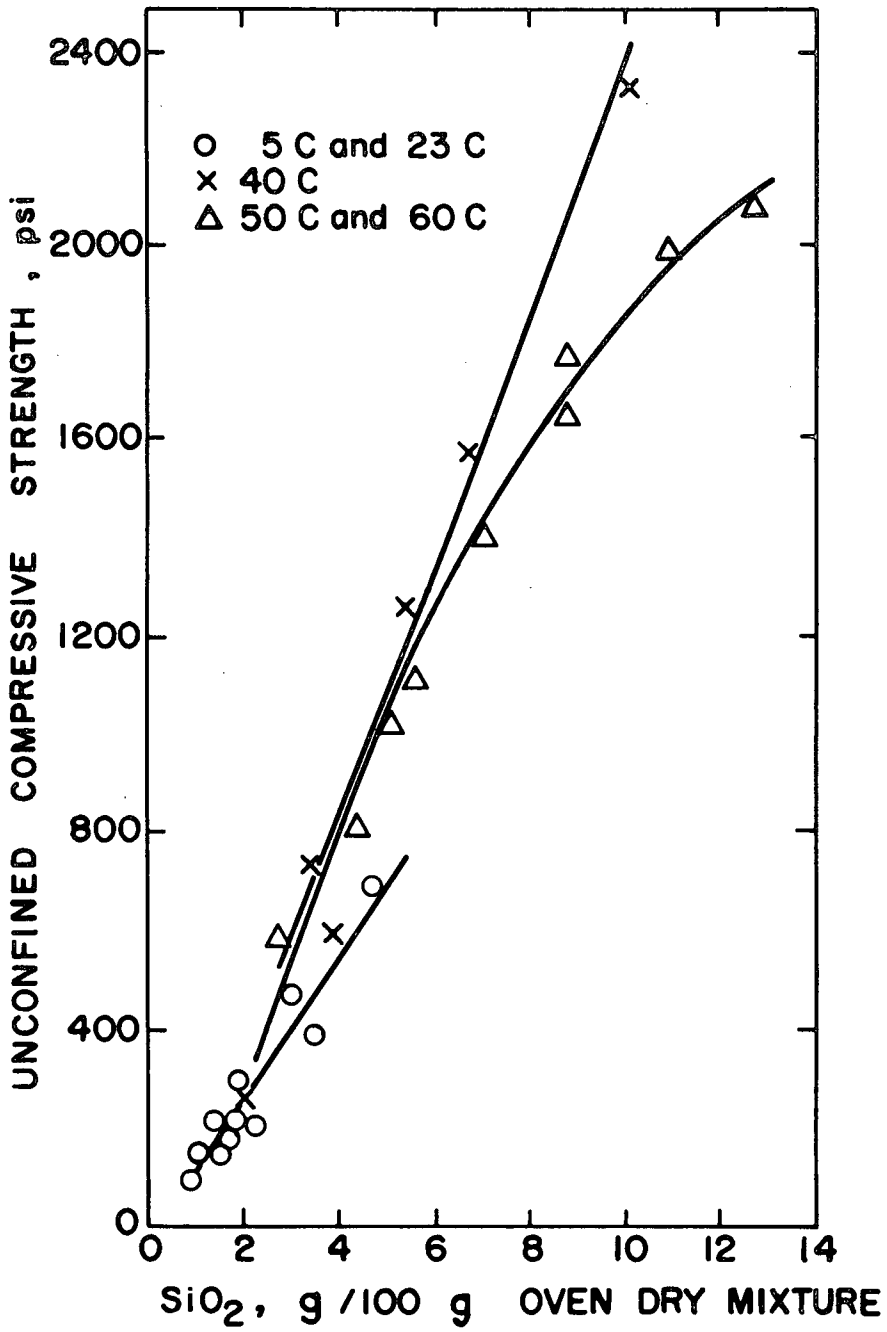
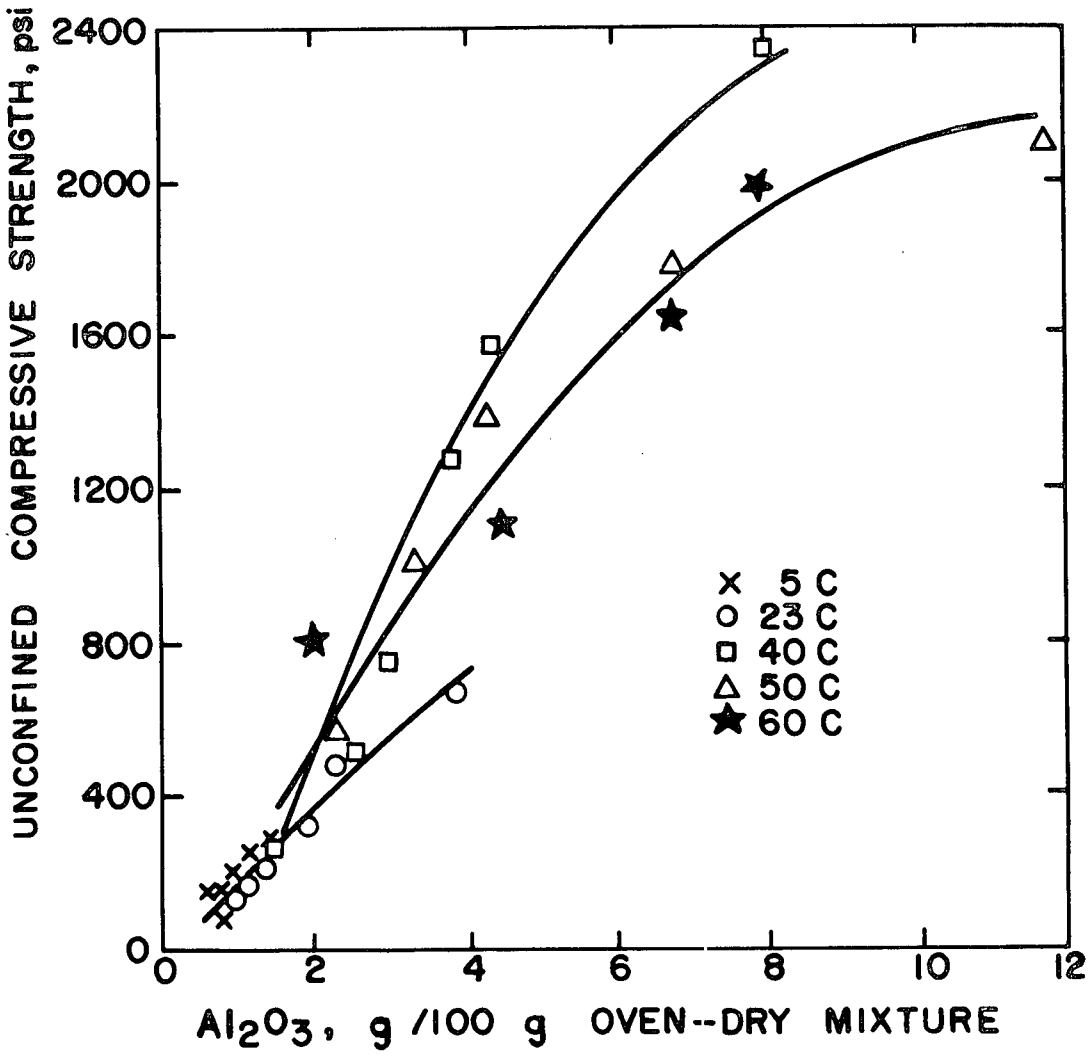

2400
2000
1600
1200
800
400
0
UNCONFINED COMPRESSIVE STRENGTH , psi
○ 5 C and 23 C
× 40 C
△ 50 C and 60 C
0
2
4
6
8
10
12
14
SiO2, g /100 g OVEN DRY MIXTURE

Figure 11. Relation between unconfined compressive strength and acid-soluble alumina in cured samples.


UNCONFINED COMPRESSIVE STRENGTH, psi
2400
2000
1600
1200
800
400
0
0
2
4
6
8
10
12
Al2O3, g /100 g OVEN--DRY MIXTURE
X 5 C
O 23 C
□ 40 C
△ 50 C
★ 60 C

different phase of the reaction responsible for strength development at 50°C and 60°C curing temperatures than at the 5°C and 23°C curing temperatures, but they do not explain the more efficient strength development in terms of acid-soluble silica and alumina with the intermediate 40°C curing temperature.

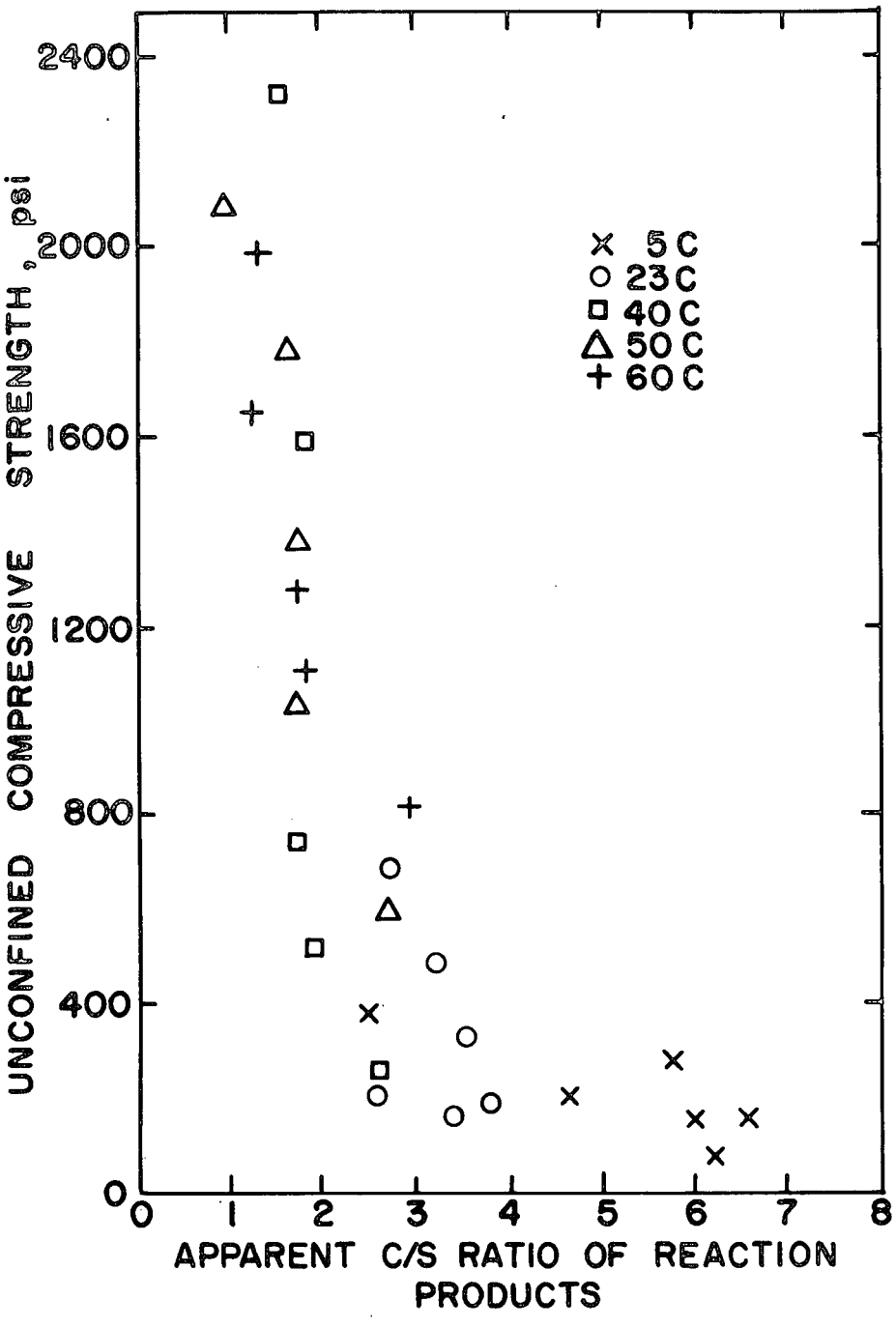
The average unconfined compressive strength as a function of apparent C/S ratio is shown in Figure 12. Although there is a large amount of scatter it is evident that for the production of high strengths it is necessary to have an apparent C/S ratio less than two.

These low C/S ratios are produced at curing temperatures of 40°C and higher (Table 2). This probably accounts for the two distinct groupings of points in Figure 1.

It also appears that the farther the consecutive reaction proceeds the lower the C/S ratio becomes and the higher goes the unconfined compressive strength (Tables 1 and 2, Figure 3).

To summarize, the compressive strength of the mixture is affected by the crystalline structure as well as the amount of reaction products formed in the lime-clay reaction. This was evident from the more efficient strength development in terms of acid-soluble silica and alumina, and disappearing calcium hydroxide at the higher curing temperatures. This increased strength development was accompanied by a change in the number of crystalline reaction products detected by X-ray analysis. It appears that the S/A ratio of the reaction products has no apparent effect on strength developing potential of the reaction products, but the C/S ratio does.

Figure 12. Relation between unconfined compressive strength and apparent C/S ratio of reaction products in cured samples.


UNCONFINED COMPRESSIVE STRENGTH, psi
2400
2000
1600
1200
800
400
0
0
1
2
3
4
5
6
7
8
APPARENT C/S RATIO OF REACTION PRODUCTS
5 C
23 C
40 C
50 C
60 C

CONCLUSIONS

Based on this investigation the following conclusions were reached:

1. The strength gain of lime-clay mixtures cured at different temperatures is due to different phases of a complex reaction.

2. This complex reaction is: Lime + clay→ CSH(gel)→ CSH(II)→ CSH(I)→ tobermorite. The farther the reaction proceeds, the higher the strength.

3. At curing temperatures of 50°C and higher, lattice substitutions take place in the structure of the calcium silicate hydrates.

4. There is no consistent relationship between time, temperature, strength and the S/A ratio of the reaction products.

5. The curing temperature has an effect on the strength developed by a given amount of silica in a cured lime-clay mixture.

6. At a given curing temperature the cured sample that has the largest amount of acid-soluble silica or alumina, will give the highest strength.

7. To achieve higher strengths the apparent C/S ratio must be less than two.

8. Abnormally high apparent C/S ratios at low curing temperatures suggest excess calcium adsorbtion onto the clay structure rather than immediate entry into a pozzolanic reaction.

9. The total S/A ratio of the lime-clay reaction products equals that of the clay mineral.

10. Alumina in the reaction products occurs mainly in C_4AH_n at all curing temperatures; at curing temperatures of 50°C or higher, some alumina may substitute isomorphously in the calcium silicate hydrate structures.

11. It is possible to determine the amount of silica and alumina in lime-clay reaction products by spectrophotometric analysis with sufficient accuracy for comparison purposes.

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